

## **Helium isotopic ratios in fluid inclusions from fluorite-rich Mississippi Valley-Type district of Asturias, northern Spain**

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Helium isotopes have been measured in fluorite and sulphides from fluorite-rich Mississippi Valley-type (MVT) deposits from Asturias, Spain, in order to assess the involvement of mantle and crust-derived volatiles in the genesis of the deposits. The  $^3\text{He}/^4\text{He}$  of the ore fluids are  $\leq 0.1 R_a$  ruling out a contribution of mantle-derived magmatic helium in the inclusion fluids. Data support a crustal source for the volatiles and is consistent with the existing basinal model for the genesis of the Asturias MVT mineralization by mixing of sedimentary brines with infiltrating superficial fluids.

Keywords: fluorite, noble gases, helium isotopes, fluid inclusions, Asturias, MVT deposits

### **INTRODUCTION**

The F–Ba (Zn–Pb) district of Asturias, northern Spain, has produced more than 15 Mt of ore since the 1970s. The deposits share the mineralogical and geochemical characteristics of Mississippi Valley-type (MVT) ores and they have many similarities with other Mesozoic F–Ba (Zn–Pb) mineral deposits in Europe, such as the Massif Central, the North Pennine Orefield and the Southwest England (Sánchez *et al.*, 2009).

The origin of fluorine in the mineralizing fluids remains an unresolved question. According to García Iglesias and Loredó (1994) the local Permian volcanic rocks are enriched in fluorine and could have been a source of fluorine in the mineralizing fluids. The age of the Villabona deposit ( $185 \pm 28$  Ma; Sánchez *et al.*, 2009) is consistent with a regional Early Jurassic hydrothermal event that appears to be coincident with the opening of the North Atlantic Ocean. Ore fluids that penetrated to mid-crust depths during extension and acquired fluorine from the contemporaneous alkaline volcanic and plutonic rocks would be expected to have an elevated  $^3\text{He}/^4\text{He}$  ra-

tio. A primary aim of this study is to evaluate evidence for mantle-derived related to alkaline igneous activity within the fluorite-rich Mississippi Valley-type deposit in Asturias.

The  $^3\text{He}/^4\text{He}$  of crustal helium is typically  $0.01\text{--}0.05 R_a$  (where  $R_a$  is the atmosphere value of  $1.386 \times 10^{-6}$ ). This is lower by several orders of magnitude than mantle-derived helium, which ranges from  $5 R_a$  up to  $50 R_a$  (Stuart *et al.*, 2003). Thus the helium isotope composition of hydrothermal fluids trapped in minerals, allows the contribution of mantle and crust-derived volatiles in the mineralizing fluids to be quantified (e.g., Stuart and Turner, 1992; Burnard and Polya, 2004; Yamamoto *et al.*, 2001). Furthermore, helium isotopes are intimately linked to heat; both  $^4\text{He}$  and heat are produced by decay of U and Th and their daughter isotopes in crustal rocks. Consequently, the flux of mantle-derived  $^3\text{He}$  is coupled to mantle heat flow and is elevated in crustal fluids from regions undergoing extensional tectonics (Nions and Oxburgh, 1983). Thus, helium isotopes in fluids have the potential to act as a tracer of past tectonic setting, and can be used to quantify the heat source in hydrothermal systems (e.g., Burnard and Polya, 2004). Here we present the helium isotopic composition of hydrothermal fluids trapped in fluorite and sulphides from the Asturias F–Ba (Zn–Pb) mineralization. The scope of this study was to evaluate the source of the volatiles, and heat, in the mineralizing fluids.

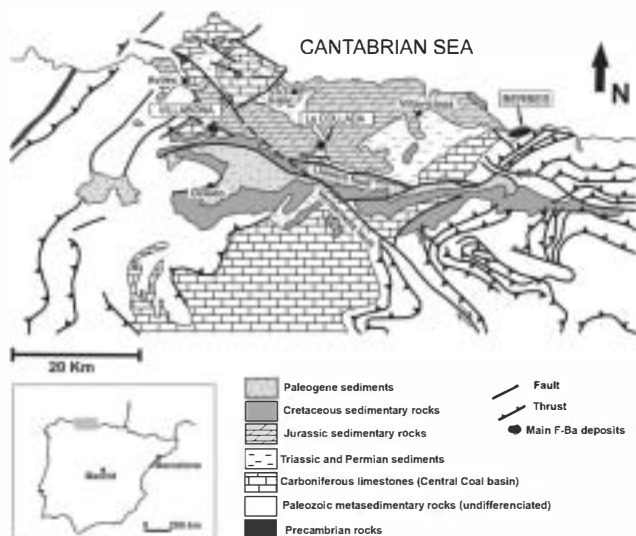


Fig. 1. Simplified map showing the location of the fluorite deposits and main mineralization districts in Asturias region: Berbes, La Collada and Villabona (modified from Sánchez *et al.*, 2009).

## ASTURIAS MINERALISATION

The Asturias Ba–Zn–Pb mineralization is exposed at three main mineralized districts; Berbes, La Collada and Villabona (Fig. 1). The mineralization mainly occurs as veins enclosed in limestones within the Paleozoic basement, and veins and stratabound bodies in highly silicified Permian–Triassic red-bed sediments (carbonates, marls and sandstones). These Permian–Triassic sediments are interbedded with basaltic to trachyandesitic lavas cropping out at the depocenter of the Permian–Triassic Villaviciosa basin (Fig. 1). The mineral paragenesis of the F–Ba (Zn–Pb) mineralization is fluorite, quartz, barite, calcite, dolomite and minor sulphides (galena, chalcopyrite, pyrite and marcasite).

Fluid inclusion data indicate that two main types of fluids were involved in fluorite precipitation: a low salinity solution (<8.5 wt% NaCl eq.) and a high salinity CaCl<sub>2</sub>-rich fluid (from 9 to 26 wt% NaCl eq.). Fluid inclusion homogenization temperatures range from 80°C to 160°C. Halogen data obtained from crush-leach experiments support the presence of at least two fluids: a high salinity-high Cl/Br and Na/Br brine formed via dissolution of halite and, a low Cl/Br and Na/Br fluid originated by dilution of a Br-enriched evaporated seawater (Sánchez *et al.*, 2009). Precipitation of ore and gangue mineral occurred where the ascending brines encountered less saline, surface-derived fluids trapped with sediments of Permian–Triassic age and basement fractures, originating stratabound and vein type deposits respectively. Mixing between metalliferous fluoride-rich brines and low-

Table 1. He concentrations and isotope composition released by *in vacuo* crushing fluorite and sulphide minerals from MVT-like mineralization in Asturias, northern Spain.

District	Sample	Mineral	<sup>4</sup> He* (×10 <sup>-7</sup> cm <sup>3</sup> STP/g)	<sup>3</sup> He/ <sup>4</sup> He (R/R <sub>s</sub> )
Villabona	VI-05-Pi1	Pyrite	0.15 ± 0.08	0.070 ± 0.054
	VI-05-02	Pyrite	0.03 ± 0.01	0.114 ± 0.090
	VI-04-07	Fluorite	2.0 ± 1.0	0.018 ± 0.014
	VI-05-FL	Fluorite	0.52 ± 0.26	0.019 ± 0.015
Berbes	BE-03-04	Fluorite	1.9 ± 0.95	0.024 ± 0.018
	BE-05-16	Pyrite	0.56 ± 0.28	0.022 ± 0.017
	BE-05-17	Pyrite	1.3 ± 0.65	0.023 ± 0.018
La Collada	CO-04-04	Galena	3.6 ± 1.8	0.002 ± 0.001
	CO-04-15	Pyrite	0.85 ± 0.42	0.021 ± 0.016
	CO-04-16	Fluorite	1.8 ± 0.9	0.019 ± 0.015

\*He contents are calculated using the mass of crushed sample less than 100 µm. A conservative (±50%) error is applied due to uncertainty in the mass of sample from which gas has been extracted

salinity groundwater or connate brines has been proposed as the most important mineralizing process in other fluorite-rich districts in Europe, such as in the North Pennine Orefield (Bouch *et al.*, 2006).

## HELIUM MEASUREMENTS

Helium isotopes have been measured in fluid inclusions in 6 sulphides (5 pyrites and 1 galena) and 6 fluorite samples at the noble gas laboratory at SUERC, Scotland. The samples have been collected from stratabound mineralization of the main districts. Mineral separates were ultrasonically cleaned in deionized water, then in acetone prior to loading approximately 1 g of each into a 10-sample hydraulic, ultra-high-vacuum crushing apparatus. The crush-released gases were initially exposed to liquid nitrogen-cooled (77°K) metal in order to remove the water. The remaining active gases were removed by exposure to two Zr–Al getters at 300°C and the residual heavy rare gases were adsorbed onto a second nitrogen-cooled charcoal trap. A cold GP50 Zr–Al getter and a third liquid nitrogen-cooled charcoal trap was employed to minimize the partial pressure of residual gases during analysis. Helium isotopes were determined using a MAP 215-50 mass spectrometer using procedures similar to those of Stuart *et al.* (2003). In this study <sup>4</sup>He was measured on a Faraday detector. Blank levels never exceeded 0.1% of sample levels and no blank correction was applied. The <sup>3</sup>He signal was measured on Burle channeltron electron multiplier in pulse counting mode; resolution was sufficient to separate the <sup>3</sup>He peak from the nearby HD-3H peak. Blank levels of the crushing procedure were extremely low; approximately 0.1 count/second. This con-

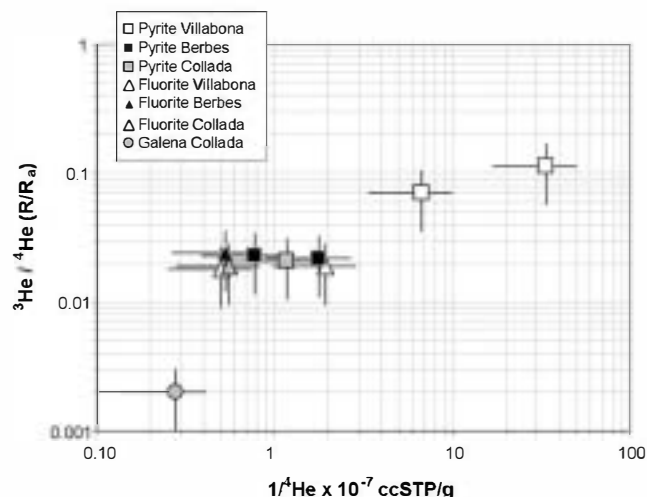


Fig. 2. Log-log plot:  $^3\text{He}/^4\text{He}$  ( $R/R_a$ ) vs.  $1/^4\text{He}$  data of pyrite, fluorite and galena samples from Asturias F-Ba (Zn-Pb) deposits. The  $^3\text{He}/^4\text{He}$  ratio is normalized to the atmosphere value of  $1.4 \times 10^{-6}$  ( $1 R_a$ ).

tributed 5–10% of measured  $^3\text{He}$  in crush extractions of the Asturias fluorite and sulphide samples, however the low measured  $^3\text{He}$  amounts have uncertainties of up to  $\pm 50\%$ .

## RESULTS AND DISCUSSION

The  $^3\text{He}/^4\text{He}$  ratios from the Asturias deposits range from  $0.021 \pm 0.016 R_a$  to  $0.114 \pm 0.09 R_a$  in pyrite, from  $0.018 \pm 0.014 R_a$  to  $0.024 \pm 0.018 R_a$  in fluorite (Table 1; Fig. 2). Most samples have  $^3\text{He}/^4\text{He}$  that are diagnostic of crustal radiogenic He and appear to rule a significant mantle He signature. Only the pyrite from Villabona (VI-05-02) has a  $^3\text{He}/^4\text{He}$  ( $0.114 \pm 0.095 R_a$ ) that is slightly higher than the value of typical crustal radiogenic He. However, it is within analytical uncertainty of the range of crustal radiogenic He values and does not present strong evidence for a significant contribution of mantle-derived magmatic helium.

*In situ* radiogenic He is a possible source of He in old minerals. The contribution is dependant on the mineral U and Th content, mineral age, and inclusion size. It has previously been shown that *in situ* radiogenic helium is unlikely to be a significant contribution to *in vacuo* crush extractions of ancient fluorite and sulphide minerals (Burnard and Poly, 2004). Specifically, previous studies of fluorite and sulphide from MVT mineralization in the United Kingdom have no significant contribution of radiogenic He (Stuart and Turner, 1992; Kendrick *et al.*, 2002a). The Asturias deposits are approximately 100 Myr younger than the North and South Pennine fluorite deposits. On the not unreasonable assumption that the U

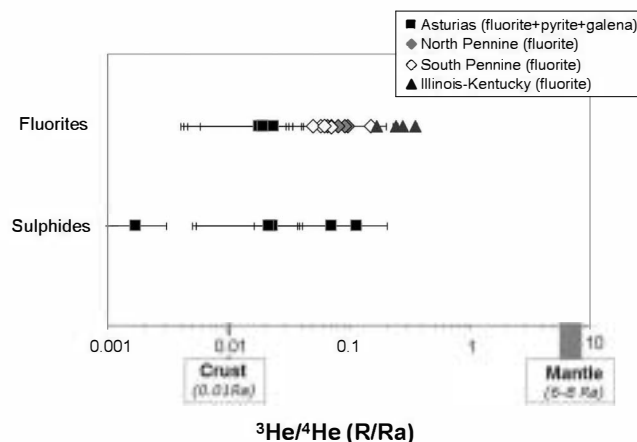


Fig. 3. Comparison of  $^3\text{He}/^4\text{He}$  ( $R/R_a$ ) of fluorite, pyrite and galena from Asturias with fluorite from North and South Pennine Orefield, UK, and Illinois Kentucky, USA (Stuart and Turner, 1992; Kendrick *et al.*, 2002a, b). The range of He isotope ratio for mantle source (6–8  $R_a$ ) assumes derivation from lithosphere- and/or upper mantle.

and Th contents of the Asturias fluorite and sulphide minerals are comparable to those of other MVT deposits it is significantly less likely that post-crystallization radiogenic He has contaminated the inclusion-hosted helium. The exception appears to be the La Collada galena (Fig. 2) that released significantly more  $^4\text{He}$  ( $3.6 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1}$ ) than the fluorite and pyrites, and is characterized by a significantly lower  $^3\text{He}/^4\text{He}$  ( $0.002 \pm 0.001 R_a$ ). This  $^3\text{He}/^4\text{He}$  is typical of radiogenic  $^4\text{He}$  produced in Li-poor minerals (e.g., Ballentine and Burnard, 2002) and it may reflect a contribution of post-crystallization radiogenic He.

The fluorite  $^3\text{He}/^4\text{He}$  ratios are slightly lower than, though overlap within uncertainty, the values measured in fluorite from the South and North Pennine Mississippi Valley-type mineralization ( $0.05\text{--}0.09 R_a$ ; Stuart and Turner, 1992; Kendrick *et al.*, 2002a; Fig. 3). This contrasts with data from fluorite-rich mineralization in the Illinois-Kentucky deposits (USA) that appears to contain a minor component of magmatic volatiles ( $^3\text{He}/^4\text{He} = 0.16\text{--}0.35 R_a$ ; Kendrick *et al.*, 2002b).

The helium isotopes do not support the involvement of a significant contribution of mantle volatiles, and therefore mantle heat, in the Asturias MVT mineralization. The age of the Villabona district fluorite ( $185 \pm 28 \text{ Ma}$ ; Sánchez *et al.*, 2009) suggests that the hydrothermal fluid movement and mineralization is coincident with Early Jurassic pre-rift thermal events. The low  $^3\text{He}/^4\text{He}$  of the mineralizing fluids provides no evidence that the fluids have a significant contribution of mantle He that appears in crustal fluid associated with active rift environments (e.g., O’Nions and Oxburgh, 1983). This in turn implies

that the mantle is not the ultimate heat source for the fluids responsible for the Asturias F–Ba (Zn–Pb) mineralization; it is unlikely that they have penetrated deep into rifting crust. This is supported by the initial Nd isotopic compositions of Villabona fluorite ( $\epsilon_{\text{Nd}}$ : –9.8 to –9.3) that implies that the metals in the mineralizing fluids were derived from sedimentary rocks rather than mantle-derived volcanics (Sánchez *et al.*, 2009). The data are consistent with a basinal brine model for genesis of the fluorite-rich mineralization where the fluids have acquired salinity from evolved seawater. Mineralization occurred when the deep saline brines mixed with the surficial fluids in carbonates, breccias and fractures resulting in the formation of veins and stratabound bodies of fluorite, barite, calcite, dolomite and quartz and sulphides. Fluid movement and mineralization took place between Late Triassic and Late Jurassic, probably coincident with rifting related to the opening of the Atlantic Ocean. This model is consistent with those derived for the formation of other fluorite-rich mineral deposits in Europe of similar age as the fluorite deposits of Chaillac, Massif Central, France (Sizaret *et al.*, 2004).

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